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POLYOLEFIN RESIN COMPOSITION

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[There are no amendments to this patent.]

(54) [Title of the invention]

Polyolefin resin composition

(57) [Abstract]

[Constitution] A polyolefin resin composition comprised of a crystalline polyolefin [A] (polypropylene) and an amorphous polyvinyl cyclohexane type resin [B], and having a composition ratio for [A] and [B] such that $[A]/[B]=95/5-5/95$ (weight ratio).
[Effect] According to the present invention, a resin composition having a high heat resistance, rigidity, and hardness as well as a low mold shrinkage factor can be produced.

[Claims of the invention]

[Claim 1] A polyolefin resin composition comprised of a crystalline polyolefin [A] (polypropylene) and an amorphous polyvinyl cyclohexane type resin [B], having a composition ratio for [A] and [B] such that $[A]/[B]=95/5\sim 5/95$ (weight ratio).

[Claim 2] The polyolefin resin composition specified in claim 1 above in which the amorphous polyvinyl cyclohexane type resin [B] can be produced by hydrogenation of the nuclei of a styrene polymer.

[Claim 3] The polyolefin resin composition specified in the claim 2 above in which the styrene polymer is a block copolymer consisting of a polymer segment mainly composed of a vinyl aromatic hydrocarbon or a polymer segment mainly composed of a conjugated diene, or a polymer composition composed of the above-mentioned block copolymer or a polymer mainly composed of a vinyl aromatic hydrocarbon.

[Claim 4] The injection-molding materials made of the polyolefin resin composition specified in claims 1-3 above.

[Detailed explanation of the invention]

[0001]

[Industrial application field] The present invention pertains to a polyolefin resin composition composed of a crystalline polyolefin and an amorphous polyvinyl cyclohexane type resin. More precisely, it pertains to a polyolefin resin composition with a high heat resistance, rigidity, and hardness, as well as a

low mold shrinkage factor.

[0002]

[Prior art] Crystalline polyolefins such as polyethylene, polypropylene, polybutene-1, poly4-methylpentene-1, and poly3-methylbutene-1 have excellent chemical resistance, electrical insulating properties, weather resistance, and they are light weight, have low moisture absorptivity, and are widely used in a variety of fields. However, the mold shrinkage factor for these materials is high, and the glass transition temperature is relatively low, thus, the heat decomposition temperature under a heavy load is low. Furthermore, their rigidity and hardness are insufficient for some applications, and an improvement is needed.

[0003]

[Problems to be solved by the invention] The objective of the present invention is to eliminate the above-mentioned problems, and to produce a polyolefin resin composition with high heat resistance, rigidity, and hardness, and which has a low mold shrinkage factor, while retaining the excellent properties of polyolefin resin compositions.

[0004]

[Means to solve the problem] As a result of the earnest efforts of the inventors to achieve the above-mentioned objective, they discovered a resin composition containing a crystalline polyolefin and an amorphous polyvinyl cyclohexane type resin that has excellent heat resistance, rigidity, hardness, and chemical resistance, and also has a low mold shrinkage factor, and

produced the present invention. Thus, the present invention is a polyolefin resin composition composed of a crystalline polyolefin [A] and an amorphous polyvinyl cyclohexane type resin [B], having a composition ratio for [A] and [B] such that $[A]/[B]=95/5-5/95$ (weight ratio).

[0005] For the composition produced by mixing a vinyl cyclohexane type resin with a crystalline polyolefin, a composition produced by mixing 10 wt% of a crystalline vinyl siloxane polymer with a melting point of 342°C with a propylene polymer is disclosed in Japanese Kokoku Patent Application No. Sho 45[1970]-32430. Also, in recent years, a propylene polymer containing 0.05-10.000 wt ppm of isotactic vinyl siloxane polymer is disclosed in Japanese Kokai Patent Application No. Sho 60[1985]-139731, etc.

[0006] Furthermore, a propylene polymer composition mixed with 0.00001-10 wt% of the hydride of a syndiotactic polystyrene is described in Japanese Kokai Patent Application No. Hei 1[1989]-131263. However, the present invention is different from substances described in the above-mentioned prior art for the following reasons. In the present invention, an improvement in the mold shrinkage factor, rigidity, hardness, mechanical strength at high temperatures, etc. is achieved through mixing with an amorphous polymer having a low mold shrinkage factor and high rigidity, hardness, and mechanical strength at high temperatures such as a vinyl cyclohexane type resin; on the other hand, in the prior art, a crystalline vinyl cyclohexane polymer

is mixed and used as a nucleating agent for crystallization of the propylene polymer. As a result, an improvement in properties, such as rigidity, hardness, and mechanical strength at high temperatures can be achieved, but the present invention is quite different from that of the prior art based on the obvious improvement achieved in the mold shrinkage factor. (On the other hand, the mold shrinkage factor increases with the increase in crystallization achieved in the prior art.)

[0007] Furthermore, for the amount used, in the prior art, the amount used is based on use as a nucleating agent, thus, the amount used is not more than 0.1 wt%, but in the present invention, the material is used as an alloy material, thus, the effect achieved is increased when at least 5 wt% of vinyl cyclohexane type polymer is used. Also, a polypropylene composition containing 0.05-10.000 wt ppm of polymer (A) produced by hydrogenation of a radical polymer or anionic polymer of the styrene derivatives shown in the following general formula:

[0008]

[Chemical formula 1]

//formula 1 here//

[0009] (In the formula, R_1 represents a hydrogen atom, or an alkyl group, R_2 represents a hydrogen atom, an alkyl group, aryl group, or a halogen atom.) is disclosed in Japanese Kokai Patent Application No. Sho 63[1988]-120751. The polymer described in

the above publication is defined as an amorphous polyvinyl cyclohexane type resin as is the case of the resin used in the present invention, but the use of the polyvinyl cyclohexane type resin in the mentioned in the above publication is intended as a nucleating agent for crystalline polyolefin as was the case for the above-mentioned crystalline vinyl cyclohexane type resin, and the amount of said resin used is very low, 10,000 wt ppm at most, and in a practical sense, 5,000 wt ppm at most.

[0010] In the following, the polyolefin resin composition of the present invention is explained in specific terms. The crystalline polyolefin [A] of the present invention is a polymer containing at least an α -olefin shown in the following general formula

[Chemical formula 2] $\text{CH}_2=\text{CHR}$

(In the formula, R represents H or an alkyl group with 1-30 carbon atoms.)

as one component, and is a crystalline substance and in specific terms, polyethylene, ethylene-butene-1 copolymer, ethylene-3-methylbutene-1 copolymer, ethylene-4-methyl pentene-1 copolymer, ethylene-hexene-1 copolymer, ethylene-vinyl acetate copolymer, ethylene-acrylic acid copolymer, and the metal salt thereof, polypropylene, propylene-ethylene copolymer, propylene-butene-1 copolymer, polybutene-1, butene-1-ethylene copolymer, butene-1-propylene copolymer, butene-1-4-methyl pentene-1 copolymer, poly4-methyl pentene-1, poly3-methyl butene-1, etc. can be mentioned, and furthermore, the above-mentioned polymers can be

mixed and used in combination. Among those listed above, polypropylene and polymers made of propylene and other olefin polymers mainly composed of propylene are especially suitable.

[0011] It is desirable for the above-mentioned crystalline polyolefin resin [A] to have a degree of crystallization of at least 10% when measured by differential scanning calorimetry. Also, the ultimate viscosity $[\eta]$ of the above-mentioned crystalline polyolefin resin [A] measured in 135°C decalin is in the range of 0.1-5 dl/g. Furthermore, the heat decomposition temperature of the above-mentioned crystalline polyolefin resin [A] (18.6 KG weight) is at least 40°C, and preferably in the range of 50-150°C.

[0012] The amorphous polyvinyl cyclohexane type resin [B] used in the present invention can be produced by hydrogenation of the nuclei of a styrene type polymer with a weight average molecular weight in the range of 50,000-400,000 described below. When the molecular weight of the said styrene type polymer is too low, the mechanical strength is inadequate. For the above-mentioned styrene type polymer, a polymer segment mainly composed of a vinyl aromatic hydrocarbon (hereinafter "segment A"), and a polymer segment mainly composed of at least one type of a conjugated diene (hereinafter "segment B"), and a vinyl aromatic hydrocarbon block copolymer containing A segment in a range of 20 wt% to 95 wt% (hereinafter simply referred to as block copolymer, in some cases), or a mixture of the two components mentioned above can be used.

[0013] For applications where impact strength is required, it is desirable to use a hydride of the above-mentioned block copolymer as component [B] or a mixture of the above-mentioned and a hydride of a vinyl aromatic hydrocarbon polymer. For examples of the above-mentioned vinyl aromatic hydrocarbon, styrene, p-methyl styrene, α -methyl styrene, etc. can be mentioned, and as a typical example, styrene can be mentioned. For examples of vinyl aromatic hydrocarbon polymer, homopolymers made of one type of the above-mentioned vinyl aromatic hydrocarbons, or copolymers made of two or more of these polymers can be mentioned.

[0014] For examples of polymers mainly composed of a vinyl aromatic hydrocarbon, the above-mentioned vinyl aromatic hydrocarbon alone, or a copolymer of the said polymer and a c polymerizable monomer, etc. can be mentioned, and it is desirable to use a copolymer produced by performing a c polymerization for these polymers within a range where the properties of the vinyl aromatic hydrocarbon is not lost. For examples of other monomers, alkoxystyrene such as methoxystyrene, and t-buthoxystyrene, methacrylates such as methylmethacrylate, and cyclohexylmethacrylate, acrylates such as ethylacrylate, maleic anhydride, N-phenylene maleimide, etc. can be mentioned.

[0015] For examples of conjugated diene included in the block copolymer, 1,3-butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene, 1,3-hexadiene, etc. can be mentioned, and in particular, 1,3-butadiene, and isoprene are commonly used. The

block copolymer made of segment A and segment B can be easily produced by a conventional method, for example, so-called living anionic polymerization, for example, a method where polymerization is performed in a hydrocarbon solvent such as hexane and heptane using an organic lithium compound as an initiator. In the case when a block copolymer alone is used as a polyvinyl cyclohexane type resin, the amount of the segment A included in the block copolymer is preferably at least 80 wt%, preferably, at least 95 wt%. In the case when the amount of the segment A included is 80 wt% or less, the heat resistance of the resin produced after the hydrogenation reaction becomes inadequate.

[0016] Furthermore, in the case when a vinyl aromatic hydrocarbon polymer hydride and block copolymer hydride are mixed and used in combination as a polyvinyl cyclohexane type resin, it is desirable to use 20 wt% or less of the component produced by performing a hydrogenation for a conjugated diene component for the total composition. Furthermore, in the case when the above-mentioned composition is used as a polyvinyl cyclohexane type resin, hydrogenation can be performed after mixing a non-hydrogenation vinyl aromatic hydrocarbon copolymer and a block copolymer.

[0017] Polyvinyl cyclohexane type resin can be produced by performing a nuclei hydrogenation reaction for the above-mentioned styrene type polymer in the presence of a hydrogenation catalyst having an aromatic hydrogenation capacity. For examples

of hydrogenation catalysts that can be used in this case, metals such as nickel, cobalt, ruthenium, rhodium, platinum, and palladium, and the oxides, salts, and complexes thereof, or the above-mentioned substances deposited on a carrier consisting of a material such as activated carbon, diatomaceous earth, alumina, and SiO_2 can be mentioned. Among those listed above, Raney nickel, stabilized nickel, ruthenium, and palladium deposited on a carrier such as carbon or SiO_2 is especially desirable from the standpoint of reactivity and easy post-treatment processes. Upon hydrogenation of vinyl aromatic block copolymer, essentially a 100% hydrogenation can be achieved for the double bonds in the conjugated diene polymer segment.

[0018] It is desirable to perform the hydrogenation reaction under a pressure of 50-250 kg/cm^2 and at a temperature in the range of 100-200°C using a saturated hydrocarbon solvent such as cyclohexane, methyl cyclohexane, n-octane, decalin, tetralin, and naphtha, or an ether type solvent such as THF. When hydrogenation is carried out for the vinyl aromatic hydrocarbon block copolymer under the above-mentioned conditions, hydrogenation of the double bond in the conjugated diene polymer segment takes place rapidly.

[0019] The degree of hydrogenation of the nuclei of the aromatic group based on the hydrogenation reaction is preferably at least 50%. When the hydrogenation ratio is too low, problems such as deterioration in the heat resistance of the resin occurs, which is not desirable. Also, in the present invention, the heat

resistance of the polyvinyl cyclohexane type resin [B] is preferably at least 100°C in terms of the heat decomposition temperature under a load of 18.6 kg. The polyvinyl cyclohexane type polymer produced in the present invention is an amorphous material. Thus, when a measurement is performed by a differential scanning calorimeter (DSC), a crystal melting peak is not observed to any significant degree.

[0020] In the present invention, the polyvinyl cyclohexane type resin (mixture) with a weight average molecular weight of 50,000-400,000 produced as described above is mixed with a crystalline polyolefin, and a resin composition is produced. As for the mixing ratio of the composition, a resin composition with properties that are further improved can be produced when the mixing ratio of crystalline polyolefin [A] and polyvinyl cyclohexane type resin [B], [A]/[B] (weight ratio) is in the range of 95/5-5/95, preferably 51/49-95/5, and especially 51/49-90/10.

[0021] In addition to the above-mentioned component [A] and component [B], the vinyl aromatic hydrocarbon polymer, a polymer produced by hydrogenation of the conjugated diene polymer segment of the block copolymer composed of a vinyl aromatic hydrocarbon polymer segment and a conjugated diene polymer segment, or an amorphous polymer such as polypheylene ether, polycarbonate, and polymethyl methacrylate listed above as raw materials for the polyvinyl cyclohexane type resin also can be included in the resin composition of the present invention at a ratio within a

range that does not interfere with the objective of the present invention. For example, phenolic type antioxidants such as tetrakis[methylene-3(3,5-di-t-butyl-4-hydroxyphenyl)-propionate]methane, β -(3,5-di-t-butyl-4-hydroxyphenyl)alkyl ester propionate, 2,2'-oxazamide bis[ethyl-3(3,5-di-t-butyl-4-hydroxyphenyl)propionate], and 1,3,5-trimethyl-2,4,6-tris(3,5-di-t-butyl-4-hydroxybenzyl)benzene, fatty acid metal salts such as zinc stearate, calcium stearate, and 12-hydroxy calcium stearate, sulfur type antioxidants such as dilaurylthiopropionate, and distearylthiopropionate, and phosphorus type antioxidants such as triphenylphosphite, etc. can be mentioned.

[0022] Furthermore, fillers such as silica, alumina, titanium oxide, magnesium oxide, aluminum hydroxide, magnesium hydroxide, calcium sulfate, potassium titanate, barium sulfate, calcium sulfite, talc, clay, mica, glass fibers, glass flakes, glass beads, calcium silicate, montmorillonite, bentonite, and polyamide fibers can be further included in the polyolefin resin composition of the present invention.

[0023] As a manufacturing method of the polyolefin resin composition of the present invention, a conventional method can be used, and a method in which the crystalline polyolefin [A], polyvinyl cyclohexane type resin [B], and other additives are mechanically mixed by an extruder, a banbury mixer, etc., or a method in which each component is first dissolved in a hydrocarbon solvent such as hexane, heptane, decane, cyclohexane, benzene, toluene, xylene, etc., and subsequently the solvent is

removed, etc. can be mentioned. The polyolefin resin composition of the present invention can be produced using a variety of conventional method, and a dramatically reduced mold shrinkage factor can be clearly observed when injection molding is used.

[0024] The polyolefin resin composition of the present invention is produced by mixing a polyvinyl cyclohexane type resin [B] having a high heat decomposition temperature and hardness, and a low mold shrinkage factor, with a crystalline polyolefin [A]; as a result, a polyolefin resin composition with a low mold shrinkage factor that retains the good properties of the crystalline polyolefin, such as high heat resistance, rigidity, and hardness, can be produced. Because of the above-mentioned properties, the polyolefin resin composition of the present invention can be widely used in a variety of fields where high heat resistance, scratch resistance, and dimensional stability are required in addition to conventional fields where crystalline polyolefin is widely used.

[0025]

[Application examples] In the following, the present invention is explained further in specific terms with application examples. Also, the measurement methods and evaluation methods used in the present invention are explained below.

(1) Melt flow index (MFR)

According to the specification of ASTM D1238, measurement was performed at the prescribed temperature under a load of 2.16 kg.

(2) Production of sample piece

An injection molding machine, J-28SA, produced by Nippon Steel Corp. (Ltd.), and a predetermined die used for sample pieces were used, and molding was performed under the molding conditions shown below. The test pieces were stored at ambient temperature for 48 hours after production; then measurements were made.

Molding conditions: Cylinder temperature 260°C, die temperature 60°C, injection pressure primary/secondary=15/12 (kg/cm²), maximum injection speed, screw rotation 120 rpm, cycle [(injection) + (pressure retention)/cooling] = 5/30 sec

(3) Bend test

Shape of the sample piece: 60 x 10 x 2.5 mm, span distance 40 mm

Test speed: 1 mm/min

Test temperature: 23°C

[0026] (4) Heat decomposition temperature (HDT)

Based on the specification of ASTM D648.

Sample test shape: 5 x 1/4 x 1/2 inches

Weight: 264 psi

(5) Pencil hardness test

Based on the specification of JIS K 5400

(6) Izod impact strength

Based on the specification of ASTM D256

(7) Mold shrinkage factor

According to the specification of ASTM D955, measurement was performed for a square sample sheet having 8 cm sides.

[0027] Application Example 1

A thorough mixing was performed for a 3.5 kg of pellet of

crystalline polyolefin (product of Sanyo Kasei Corp., (Ltd.), 4700 JP, crystallization of 61%, MFR (at 236°C) of 15/10 min) used as component [A], and 1.5 kg pellet of polyvinyl cyclohexane type resin (hydrogenation ratio of 100%, weight average molecular weight of 180,000) produced by nuclei hydrogenation of a styrene homopolymer (product of Mitsubishi Monsanto Kasei Corp., YG-66, weight average molecular weight of 200,000) used as component [B], hot-melt mixing was performed by a biaxial extruder (Ikegai Iron and Steel Corp. (Ltd.), PCM36) at a cylinder temperature of 260°C, and formed into a pellet by a pelletizer. The pellet produced was made into a sample piece using the above-mentioned method, and the properties were evaluated. Also, when measurement of the above-mentioned polyvinyl cyclohexane type resin was done using DSC, a crystalline melting peak was not observed. Measured results obtained for each of the properties are shown in the following Table I.

[0028] Application Example 2

In Application Example 1, a hydrogenated block copolymer (weight average molecular weight of 114,000, nuclei hydrogenation ratio of 100%) of styrene-butadiene block copolymer (weight average molecular weight of 120,000, butadiene content of 15 wt%) . produced by an anionic polymerization reaction was added as component [B], and a resin composition was produced as in Application Example 1. Also, when measurements were made for the above-mentioned polyvinyl cyclohexane type resin using DSC, a crystalline melting peak was not observed. Results of

measurements for each of the properties are shown in Table I.

[0029] Application Example 3

In Application Example 1, the nuclei hydrogenation ratio was changed to 85%, and a resin composition was produced as in Application Example 1. Results of measurements for each of the properties are shown in Table I.

Application Example 4

In Application Example 3, the ratio of the component [A] and component [B] was changed to 8:2, and a resin composition was produced as in Application Example 3. Results of measurements for each of the properties are shown in Table I.

Application Example 5

In Application Example 1, 4-methylpentene-1 polymer (product of Mitsui Petrochemical Corp., RT-18, crystallization 40%, MFR (250°C, 5 kg load)=26 g/10 min) was used as component [A], and a resin composition was produced as in Application Example 1. Results of measurements for each of the properties are shown in Table I.

[0030] Comparative Example 1

The properties of polypropylene (4700T) used in Application Example 1 are shown in Table I.

Comparative Example 2

The properties of 4-methylpentene-1 polymer (RT-18) used in Application Example 5 are shown in Table I.

Comparative Example 3

In Application Example 1, the amount of crystalline polyolefin was changed to 5.0 kg, and the amount of the polyvinyl cyclohexane resin was changed to 5 g, and the polypropylene and polyvinyl cyclohexane were both blended in the form of powders, and pelletization and molding were performed as in Application Example 1. The amount of polyvinyl cyclohexane resin included was 1000 ppm. The results obtained are shown in Table I. As shown in Table I, the improvement in the rigidity, and heat resistance achieved was insignificant; furthermore, an increase in the mold shrinkage factor is observed.

[0031]

[Table I]

Table I

	Flexure strength (kg/cm ²)	Bend modulus (kg/cm ²)	HDT (°C)	Izod impact strength (kg·cm/cm)	Mold shrinkage factor (%) (MD/TD)	Pencil hardness
Application Example 1	510	17500	104	2	0.96/1.10	B
Application Example 2	503	15100	95	3	0.98/1.15	3B
Application Example 3	520	17700	94	2	0.95/1.10	B
Application Example 4	480	16000	79	2	1.23/1.13	B
Application Example 5	500	17000	112	2	1.61/1.30	2B
Comparative Example 1	415	14200	63	3	1.39/1.61	3B
Comparative Example 2	360	13000	90	3	2.60/1.91	3B
Comparative Example 3	480	14800	72	3	1.45/1.68	2B

[0032]

[Effect of the invention] According to the present invention, it is possible to produce a polyolefin resin composition with a high heat resistance, rigidity, and hardness, as well as a low mold shrinkage factor.

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